

(51) **FEDERAL REPUBLIC OF GERMANY**

Int. Class.: C 07 c
B 01 j

GERMAN PATENT OFFICE

(52) German Class.: 12 q 14/02
12 o, 10
12 g, 4/02

(10) **Patent Specification 1 443 329**
(11)

(21) File number: P 14 43 329.5-42 (S 78437 IV b)

(22) Application date: March 12, 1962

(43) Disclosure date: ---

(44) Laid out for inspection on: January 2, 1970

Issue priority: ---

(30) Joint priority:

(32) Date: January 10, 1962

(33) Country: Italy

(31) File number: 15295

(54) Description: A method and device for the continuous catalytic separation of alkyl aryl hydro peroxides and particularly of cumene hydro peroxide with sulfuric acid.

(41) Supplement for: ---

(42) To be removed from: ---

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(56) Documents taken into account to determine the patentability:

DT-AS 1 016 270 F.A. Henglein, Basics of Chemical

DT-AS 1 064 955 Technology, 1949

DT-AS 1 112 527 Page 79, Figure 79 a

Ullmann's Encyclopedia of Industrial
Chemistry, 3rd edition, Vol. 1, 1951,
Pages 227 and 228

ORIGINAL INSPECTED

12.69 909 581/116

The invention concerns a method for the continuous catalytic separation of alkyl aryl hydro peroxides and particularly of cumene hydro peroxide with sulfuric acid in a homogenous reaction medium to form the respective phenols and carbonyl compounds while cooling the reaction mixture in a heat exchanger to dissipate the reaction heat and the invention also concerns a device to realize such a method.

To achieve high phenol and ketone yields with these methods, it will be necessary to carefully control the separating temperature, since the formation of secondary products increases tremendously and thus decreases the yield and since the processing of the reaction mixture becomes more difficult. The separation process may even become explosive, when the temperature increases too much.

Many attempts have been made to find solutions for the problems that occur in these very strong exothermal reactions, i.e., particularly with respect to controlling the reaction temperature; some of them were indeed successful to a certain degree, but none of them was really satisfactory.

The German patent specification 1 016 270, for example, describes a method that uses a reaction vessel fitted with a stirring and cooling device, in which a phenol that corresponds to the phenol formed during the separation to be performed is supplied and preheated; this is followed by a simultaneous yet separate supply of the hydro peroxide to be separated and of the sulfuric acid to serve as the separation catalyst and to simultaneously and continuously remove a corresponding quantity of the reaction mixture. Although this method produces relatively high yields, it is not considered very satisfactory, particularly because the phenol yield varies very much for unexplainable reasons, i.e., it varies between 92% and 97%.

The German patent specification 1 112 527 describes a method that is superior to the above-described method in that respect; however, it is not that favorable with respect to the absolute yield quantity and particularly with respect to the expensive equipment that is needed. Although it is true that the reaction temperature can be maintained accurately at $\pm 2^\circ$ with this method, this requires a series of reaction vessels and heat exchanger units fitted with expensive control devices. Furthermore, it is possible to use only strongly diluted reaction components such as a 1% to 5% aqueous sulfuric acid, thus making the reaction mixture heterogenous and making it necessary to fit all reaction vessels with effective stirring devices.

Accordingly, the task of the invention consists in the development of a method that overcomes the disadvantages of the known methods, particularly with the use of relatively few devices, and that also makes it possible to achieve an accurate and reliable control of the reaction temperature with the use of concentrated starting materials and to achieve high yields in a reliable manner and without major fluctuations.

This task is solved with a method for the continuous catalytic separation of alkyl aryl hydro peroxide and particularly of cumene hydro peroxide with sulfuric acid in a homogenous reaction medium to form the respective phenols and carbonyl compounds while cooling the reaction mixture in a heat exchanger to dissipate the reaction heat, characterized by the fact that the reaction

mixture is circulated through the heat exchanger and that fresh alkyl aryl hydro peroxide is added, in which case the circulation velocity of the circulating mixture is between ten and several hundred times higher than the supply velocity of the hydro peroxide measured in volume units per time unit.

In accordance with the invention, the reaction mixture is thus circulated through a heat exchanger, in which case fresh hydro peroxide is added at a supply velocity that is given in volume units per time unit and that is substantially lower than the circulation velocity of the circulating mixture. By changing this ratio accordingly, the reaction temperature can be easily maintained between the desired levels.

Furthermore, the above-mentioned invention concerns a device that permits continuous separation of alkyl aryl hydro peroxides to form the respective phenols and ketones and that consists of a heat exchanger, whose ends are - through a circulation pipe - connected to a circulation pump for the decomposition mixture to form a closed circulation system, also consists of supply lines for the hydro peroxide and the decomposition catalyst and has means to draw the reaction mixture from the circulation system at a ratio in relation to the supplied hydro peroxide and the catalyst.

Figures 1 and 2 give a schematic representation of two design samples of such a device used to realize the method in accordance with the invention.

In the device shown in Figure 1, A is a heat exchanger of the tube-bundle type, B is a circulation pipe and C is a circulation pump.

To increase the flow velocity of the reaction mixture, expressed in length units per time unit, at the inlet of pipes 1 and 2 for the hydro peroxide or the sulfuric acid, the diameter of circulation pipe B is selected substantially smaller than the diameter of heat exchanger A, i.e., at least at this location.

When putting the device into operation, a mixture that has already been separated is supplied through pipe 1 and is then quickly circulated through pump C.

The mixture is brought to the selected circulation temperature by supplying heat exchanger A with hot water through pipes 4 and 5. As soon as the selected circulation temperature was reached, concentrated sulfuric acid is fed with the help of the hydro peroxide solution and through pipe 2.

The released reaction heat is fully dissipated from the reaction mixture while in heat exchanger A, in which cooling water now circulates. The reaction mixture is removed through pipe 3 at a quantity in relation to the supplied quantity.

The temperature of the reaction mixture can be maintained within a few degrees Celsius by correspondingly setting the ratio between the flow velocity of the reaction mixture circulating in the device and the supply velocity of the hydro peroxide.

The flow velocity is approximately ten to several hundred times greater than the supply

velocity of the hydro peroxide, i.e., as a function of the hydro peroxide type and concentration.

The reaction can be performed at any pressure or vacuum.

According to a preferred design, the hydro peroxide is separated at a concentration of more than 70% by weight, at a ratio of 100:1 to 500:1 between the flow velocity and supply velocity, at a temperature of between 70 °C and 80 °C and under atmospheric pressure.

Since the concentration of the reactants are selected at a low level and the temperature control is very accurate, the device in accordance with the invention is very simple and safe to operate.

Figure 2 shows a second design form that is particularly suited for separating hydro peroxides, whose separation produces volatile ketones such as cumene hydro peroxide.

When using this device and operating it in a vacuum, it is possible to achieve an almost complete ketone distillation from the reaction mixture by taking advantage of the reaction heat.

To the device that is shown in Figure 2 and is filled with a mixture that has already been separated, contains no acetone and is heated to 100 °C, one adds cumene hydro peroxide through pipe 8 and preferably at a concentration of more than 70% by weight, and adds sulfuric acid as separation catalyst through pipe 7.

When the quantity of the water formed during the separation of cumene hydro peroxide amounts to less than 6% in the mixture, a sufficient water quantity is added through pipe 6 to bring the water percentage content to 6%. This lowers the boiling point of the mixture and promotes the acetone evaporation.

The separation is instantaneous. The reaction vessel is continuously evacuated to a pressure of approx. 400 Torr with the help of a jet pump (an ejector), to which it is connected through pipes 9, 11, 12 and 14.

The reaction mixture is relieved and partly evaporated in vessel E, in which case some of the reaction heat is dissipated. The vapors flow through pipe 9, mist separator 10 and then through pipe 11 to reach cooling unit H, where they are liquefied with circulating water (pipes 17, 17a) and collected in liquid form in tank I.

Between 85% and 90% of the acetone produced with the separation of hydroxy-peroxide is obtained from tank I through pipe 13 and suction pump M, i.e., at a concentration of approx. 10%, in which case the remaining 10% consists of other reaction products and particularly of cumene and water. A reaction mixture that contains almost no ketone is removed from tank E through pipe 15 and pump L. In heat exchanger D that is cooled with cooling water (pipes 16, 16a), the reaction heat is almost completely removed from the circulating reaction mixture, since the acetone evaporation consumes less than one-third of the reaction heat. As for the rest, reference is hereby made to the description of the device shown in Figure 1. The pressure in the reaction tank can vary between a few Torr and the atmospheric pressure.

The following example explains the invention.

Example

In a device according to Figure 1 that is filled with 500% by weight of a mixture obtained from a previous separation phase, this mixture is circulated with the help of pump C in such a manner that the circulation velocity measured at any point of pipe B is 200,000% by weight or approx. 210,500 volume parts per hour.

Heat exchanger A is supplied with water at a temperature of 90 °C through pipe 4-5 until the temperature of the circulating mixture has reached 70 °C. After reaching this temperature, the hot water at 90 °C is replaced with warm water at 25 °C, while one starts to add simultaneously and through pipe 1, 970 volume parts (1000% by weight) to a solution of cumene hydro peroxide in cumene (hydro peroxide content = 81.9% by weight) and 2 parts by weight per hour of commercially available concentrated sulfuric acid (98%) through pipe 2, corresponding to a ratio of approximately 217 between the flow velocity of the circulating mixture and the feed velocity of the hydro peroxide. A reaction mixture quantity of 1002 parts by weight per hour is removed continuously through pipe 3.

The cumene hydro peroxide content in the reaction mixture remained below 0.1% by weight through the whole test duration (72 hours).

The unreacted mixture was left in the device at the end of the test for a later re-use.

The temperature was kept between 70 °C and 72 °C during the whole test duration, in which case the atmospheric pressure was maintained.

The obtained mixture was neutralized with the help of ion-exchange resins and was then divided into its components through distillation.

The phenol yield was 98% of the theoretical value and that of acetone was 96% of the theoretical value.

Patent claims

1. A method for the continuous catalytic separation of alkyl aryl hydro peroxides and particularly of cumene hydro peroxide with sulfuric acid in a homogenous reaction medium to form the respective phenols and carbonyl groups while cooling the reaction mixture in a heat exchanger to dissipate the reaction heat, characterized by the fact that the reaction mixture is circulated through the heat exchanger and fresh alkyl aryl hydroxy-peroxide is added, in which case the flow velocity of the circulating mixture is between ten and several hundred times greater than the feed velocity of the hydro peroxide, i.e., measured in volume parts per time unit.

2. A method in accordance with claim 1, characterized by the fact that the ketone obtained during the separation process is almost completely distilled from the mixture while taking advantage of the reactor heat.

3. A device that is designed for the continuous separation of alkyl aryl hydro peroxides to form the respective phenols and ketones according to claims 1 and 2 and that consists of a heat exchanger, whose ends are - through a circulation pipe - connected to a circulation pump for the decomposition mixture to form a closed circulation system, consists of supply pipes for the hydro peroxide and the decomposition catalyst and also has means to draw the reaction mixture from the circulation system at a ratio to the supplied hydro peroxide and the catalyst.

4. A device in accordance with claim 3, characterized by the fact that a section of the circulation pipe has a diameter that is smaller than that of the heat exchanger, in which case the feed pipes enter at that section of the circulation pipe.

5. A device in accordance with claim 3, characterized by the fact that the circulation pipe runs through a blow tank that is connected to a suction and liquefaction tank for the volatile decomposition products.

One page with drawings forms a part of this document

DRAWING PAGE NO.:

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| Number: | 1 443 329 |
| Int. Class.: | C07c |
| German Class.: | 12 q 14/02 |
| Inspection date: | January 2, 1970 |

Figure 1

TO THE EJECTOR

Figure 2